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- (54) ETCHING SOLUTION, ETCHED ARTICLE AND METHOD FOR ETCHED ARTICLE
- (57) An etching solution which contains hydrogen fluoride (HF) and exhibits an etching rate ratio: etching

rate for a boron-glass film (BSG) or boron-phosphorus-glass (BPSG)/etching rate for a thermally oxidized film (THOX) of 10 or more at 25°C.

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Description

TECHNICAL FIELD

[0001] The present invention relates to an etching solution, a method for producing an etched article and an etched article produced by the method, more specifically, an etching solution and a method for producing an etched article for selectively etching a doped oxide film, particularly BSG or BPSG relative to an undoped oxide film, particularly THOX, and an etched article produced by the method.

10 BACKGROUND ART

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[0002] Conventionally, as etchants for silicon wafers and the like have been used buffered hydrofluoric acids comprising HF (50% by weight) and NH_4F (40% by weight) at such a ratio that can achieve a desired etch rate.

[0003] However, the buffered hydrofluoric acids etch not only doped oxide films such as BSG films, BPSG films, phosphosilicate glass (PSG) films, arsenic silicate glass (AsSG) films and the like, but also undoped oxide films such as USG including TEOS (oxide obtained by CVD method using tetraethoxysilane gas) films, THOX and the like. Therefore, the buffered hydrofluoric acids can not selectively etch the doped oxide films.

[0004] An object of the present invention is to provide an etching solution and an etching method for selectively etching oxide films doped with impurities relative to TEOS and THOX.

DISCLOSURE OF INVENTION

[0005] The present invention relates to the items 1-16 listed below.

25 Item 1: An etching solution comprising hydrofluoric acid, wherein an a ratio of etch rate of a boron silicate glass film (BSG) or boron phosphosilicate glass / an etch rate of a thermal oxide film (THOX) at 25°C is 10 or higher. Item 2: The etching solution according to item 1, wherein a solvent in the etching solution has a relative dielectric constant of 61 or lower.

Item 3: The etching solution according to item 1, the solution containing at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom.

Item 4: The etching solution according to item 1, the solution containing (i) water and (ii) at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom, the water being contained in a concentration of 70% by weight or lower.

Item 5: The etching solution according to item 1, wherein the weight ratio of HF: isopropyl alcohol: water is 0.1-50% by weight: 30-99% by weight: 0-70% by weight.

Item 6: The etching solution according to item 1, wherein the weight ratio of HF: acetic acid: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.

Item 7: The etching solution according to item 1, wherein the weight ratio of HF: tetrahydrofuran: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.

Item 8: The etching solution according to item 1, wherein the weight ratio of HF: acetone: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.

Item 9: The etching solution according to item 1, wherein the weight ratio of HF: methanol: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.

Item 10: The etching solution according to item 1, wherein the weight ratio of HF: ethanol: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.

Item 11: The etching solution according to item 1, the solution comprising an inorganic acid.

Item: 12 The etching solution according to item 11, wherein the inorganic acid has a pKa value at 25°C of 2 or lower.

Item 13: The etching solution according to item 11, wherein the weight ratio of HF: HCI: water is 0.01-50% by weight: 1-36% by weight: 0-99% by weight.

Item 14: The etching solution according to item 11, wherein the weight ratio of HF: HNO₃: water is 0.01-50% by weight: 1-70% by weight: 0-99% by weight.

Item 15: A method for producing an etched article by etching an article to be etched with the etching solution as defined in any of items 1-14.

Item 16: An etched article which is obtainable by the method of item 15.

[0006] According to the etching solution of the invention, the ratio of BSG etch rate / THOX etch rate and/or the ratio of BPSG etch rate / THOX etch rate at 25°C is/are 10 or higher, preferably 20 or higher, more preferably 50 or higher, particularly 100 or higher.

[0007] In case of using TEOS instead of THOX, the ratio of BSG etch rate / TEOS etch rate and/or the ratio of BPSG etch rate / TEOS etch rate at 25°C is/are 5 or higher, preferably 10 or higher, more preferably 50 or higher, particularly 100 or higher.

[0008] The etch rate of the etching solution of the invention can be calculated as the difference in thickness of a film (BSG; BPSG; THOX; TEOS and like USG, etc.) before and after etching divided by etch time.

[0009] The water content is not higher than 70% by weight, preferably not higher than 30% by weight, more preferably about 30-5% by weight. The relative dielectric constant of the etching solution expresses an arithmetic mean of the relative dielectric constants of the components of the etching solutions other than the HF and inorganic acid.

[0010] Preferable examples of the inorganic acid include inorganic acids having a pKa value at 25°C of 2 or lower, for example, hydrochloric acid (pKa =-8), nitric acid (pKa=-1.8), hydrobromic acid (pKa=-9), hydroiodic acid (pKa=-10) and perchloric acid (a pKa-unmeasurably strong acid).

[0011] Examples of the organic acid include acetic acid (relative dielectric constant: 6.15 (20°C)), propionic acid (relative dielectric constant: 3.4 (40°C)), butyric acid (relative dielectric constant: 2.97(20°C)), isobutyric acid (relative dielectric constant: 2.63(71°C)), caprylic acid (relative dielectric constant: 2.63(71°C)), caprylic acid (relative dielectric constant: 2.45(20°C)), monochloroacetic acid (relative dielectric constant: 21 (20°C)), dichloroacetic acid (relative dielectric constant: 4.6 (60°C)), monofluoroacetic acid, difluoroacetic acid, trifluoroacetic acid, α -chlorobutyric acid, β -chlorobutyric acid, α -chlorobutyric acid, acrylic acid and like monocarboxylic acids, methanesulfonic acid, toluenesulfonic acid and like sulfonic acids, oxalic acid, succinic acid, adipic acid, tartaric acid, citric acid and like polycarboxylic acids.

[0012] Examples of the organic solvent having a hetero atom include methanol (relative dielectric constant: 32.6 (25°C)), ethanol (relative dielectric constant: 24.6 (25°C)), isopropanol (IPA, relative dielectric constant: 19.9 (25°C)), 1-propanol (relative dielectric constant: 22.2 (25°C)), 1-butanol (relative dielectric constant: 17.1 (25°C)), 2-butanol (relative dielectric constant: 15.5 (19°C)), t-butanol (relative dielectric constant: 11.4 (19°C)), 2-methyl-1-propanol (relative dielectric constant: 17.95 (20°C)), 1-pentanol (relative dielectric constant: 13.9 (25°C)), 1-hexanol (relative dielectric constant: 13.3 (25°C)), 1-heptanol, 4-heptanol, 1-octanol (relative dielectric constant: 10.34 (20°C)), 1-nonyla-Icohol, 1-decanol, 1-dodecanol and like alcohols; ethylene glycol (relative dielectric constant: 37.7 (20°C)), 1,2-propanediol (relative dielectric constant: 32.0 (20°C)), 2,3-butanediol, glycerin (relative dielectric constant: 42.5 (25°C)) and like polyols, acetone (relative dielectric constant: 20.7 (25°C)), acetylacetone, methyl ethyl ketone (relative dielectric constant: 18.51 (20°C)) and like ketones; acetonitrile (relative dielectric constant: 37.5 (20°C)), propionitrile (relative dielectric constant: 29.7 (20°C)), butyronitrile (relative dielectric constant: 20.3 (20°C)), isobutyronitrile (relative dielectric constant: 20.4 (20°C)), benzonitrile (relative dielectric constant: 25.2 (25°C)) and like nitriles; formaldehyde, acetaldehyde, propionaldehyde and like aldehydes; ethylene glycol monomethyl ether, ethylene glycol monoethyl ether and like alkylene glycol mono alkyl ethers; tetrahydrofuran (relative dielectric constant: 7.6 (25°C)), dioxane (relative dielectric constant: 2.2 (25°C)) and like ethers, trifluoroethanol, pentafluoropropanol, 2,2,3,3-tetrafluoro propanol and like fluorine alcohols, sulfolane (relative dielectric constant: 43.3 (20°C)), nitromethane (relative dielectric constant: 35.87 (30°C)) and the like.

[0013] The relative dielectric constant of water is 78.3 (25°C).

[0014] The content of HF is about 0.01-50% by weight, preferably about 1-5% by weight.

[0015] The water content is not higher than 70% by weight, preferably not higher than 30% by weight, more preferably about 0-5% by weight.

[0016] The content of the inorganic acid is about 1-99% by weight, preferably about 30-70% by weight.

[0017] The content of the organic acid is about 30-99.9% by weight, preferably about 70-99.9% by weight.

[0018] The content of the organic solvent having a hetero atom is about 30-99.9% by weight, preferably about 70-99.9% by weight.

[0019] The content of at least one member selected from the group consisting of the inorganic acid, organic acid and organic solvent having a hetero atom is about 30-99.9% by weight, preferably about 70-99.9% by weight.

[0020] The inorganic acid has a pKa at 25°C of about 2 or lower, preferably about -5 or lower.

[0021] The relative dielectric constant of the organic acid and organic solvent having an hetero atom is preferably about 40 or lower, more preferably about 10 or lower.

[0022] As the HF is usually used dilute hydrofluoric acid (50 wt. % aqueous solution). However, when the HF does not contain water, 100% HF may be also used.

[0023] In case of HCI, HBr and HI, an anhydrous etching solution can be prepared by blowing these gases through the etching solution.

[0024] Preferable etching solutions of the present invention and their compositions are shown below.

- HF: IPA: water = 1-10% by weight: 70-99% by weight: 0-30% by weight
- HF: acetic acid: water = 0.5-5% by weight: 70-99.5% by weight: 0-30% by weight

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- HF: HCI: water = 0.01-5% by weight: 1-36% by weight: 50-99% by weight
- HF: nitric acid: water = 0.01-5% by weight: 1-70% by weight: 20-99% by weight
- HF: acetone: water 1-10% by weight: 70-99% by weight: 0-30% by weight
- HF: THF: water = 1-10% by weight: 70-99% by weight: 0-30% by weight
- HF: methanol : water = 1-10% by weight : 70-99% by weight : 0-30% by weight
- HF: ethanol: water = 1-10% by weight: 70-99% by weight: 0-30% by weight

[0025] The etching solution of the invention can be suitably used for selectively etching a doped oxide film of an article to be etched comprising an oxide film (BSG, BPSG, etc.) doped with B, P and the like and an undoped oxide film such as THOX, TEOS and like.

[0026] In the etching method of the present invention, the temperature of the etching solution is about 15-40°C.

[0027] Examples of the article to be etched include single crystalline silicon wafers, gallium-arsenic wafers and like wafers, especially the articles comprising a doped oxide film (BSG, BPSG, etc.) and an undoped oxide film (THOX, TEOS and like USGs).

⁵ [0028] The BSG etch rate of the etching solution of the invention is usually about 10-2000 nm/min, preferably about 40-500 nm/min.

[0029] The present invention can provide an etching solution which can selectively etch films doped with impurities, such as BSG, BPSG and the like, relative to THOX, TEOS and like USG, a method for producing an etched article using the etching solution and an etched article.

BEST MODE FOR CARRYING OUT THE INVENTION

[0030] The present invention will be explained in more detail with referring to Examples and Comparative Examples below.

Examples 1-2 and Comparative Examples 1-4 (inorganic acid)

[0031] Etching solutions were prepared by mixing HF, water, an organic solvent having a hetero atom (isopropyl alcohol (iPA), THF, acetone, methanol, ethanol), an organic acid (acetic acid) and inorganic acid (HCI, HNO₃) in the ratios shown in Table 1. Test substrates were produced by forming each of a thermal oxide (THOX) film, USG (TEOS) film, boron silicate glass (BSG) film and boron phosphosilicate glass (BPSG) film on a silicon substrate by CVD method using a tetraethoxysilane gas. The etch rate and etch selectivity of the etching solutions on the test substrates were determined.

[0032] In addition, the etch rate and selectivity of conventional HF-H₂O and HF-NH₄F-H₂O etching solutions were determined in the above-mentioned manner as Comparative Examples.

[0033] The etch rate was determined by measuring the thickness of the films before and after etching with an Auto EL-III ellipsometer manufactured by Rudolf Research.

[0034] The etch rates of the etching solutions were calculated as the difference in thickness of films before and after being etched at 25°C divided by etch time.

[0035] The results of the etching solutions with each composition are shown in Table 1 to Table 8.

[0036] The relative dielectric constant is that of a solvent (an organic solvent having a hetero atom or an organic acid) + water at 25°C, expressed as a calculated value of an average of the relative dielectric constants of the solvent and water having the particular composition.

[0037] Average of relative dielectric constants = [78.3 x (percentage by weight of water) + (relative dielectric constant of solvent at 25°C) x (percentage by weight of solvent)] / [(percentage by weight of water) + (percentage by weight of solvent)]

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12 8.5 7.3 40 27 19 10

BPSG /TEO S sele ctiv ity

BSG/ TEOS sele ctiv ity

	Sol-	Relative	HE	Water	Solvent	Relative	THOX	TEOS	BSG	BPSG	BSG/	BPSG
	vent	dielectric	-uou	-uoo	(IPA)	dielectric	etch	etch	etch	etch	THOX	/THO
		constant of	cen-	cen-	-conco	constant of	rate	rate	rate	rate	sele	×
		solvent	tra-	tra-	tration	solvent	(A/m	(A/m	(A/min	(A/m	ctiv	sele
			tion	tion	*	(IPA)+water	1n.)	in.)	•	in.)	ity	ctiv
			(8)	(%)		(calculated						1ty
				-		value)						
Ex. 1	IPA	19.9	2	S	96	23.0	12	11	370	330	31	28
Ex. 2	IPA	19.9	3	25	2	35.3	55	9/	920	1160	17	21
Ex. 3	IPA	19.9	ß	45	20	47.6	76	140	1190	1650	17	17
Ex. 4	IPA	19.9	'n	65	30	59.9	140	200	1450	1950	20	14
Ex. 5	IPA	19.9	m	m	94	21.7	7	ო	120	,	09	:
Ex. 6	IPA	19.9	10	10	80	26.4	59	82	2200	'	37	ı
Ex. 7	IPA	19.9	15	15	20	30.2	350	230	6500	,	28	1
Ex. 8	IPA	19.9	20	20	9	34.5	820	1200	12000	1	15	,
Comp.	(Water	(78.3)	1	66	0	•	58	63	380	,	6.5	,
Ex. 1	_				-							
Comp.	(Water	(78.3)	7	98	0	1	120	190	750	ı	6.3	1
Ex. 2	^											
Comp.	(Water	(78.3)	ო	95	0	•	300	490	1980	1	9.9	1
Ex. 3	^											

					_		_							-												
BPSG/	TEOS	tivit	>		•		54	; -	25	ď	3.	ı		1	,		•	,		,	ı	ı	•	,		•
BSG/T	EOS	tivit	>				38)	67	73	!	19		80	84		9	70	2	41		;	14	0	;	8.2
BPSG/	THOX	tivit	٨				75		78	26	•	ı		,	ı	•		,		,	,					ı
BSG/T	selec	tivit	>-	·			53		100	94		100	,	011	120		26	68		9	S.	3	21	17		14
BPSG	etch	(A/mi	n.)				750		940	1300	:	,	\ -	1	,	•		ı		ı	,			,		,
BSG	etch	(A/mi					530		1200	1600		2600	000	2000	4 600		0068	1 600		1300	970	,	830	670		290
TEOS	rate	(A/mi	 				14		78	22		33	4	ۍ, ٿ	55	,	0.51	23		32	46		88			72
THOX	rate	(A/mi	.: .:				10	,	12	17		_ 52 _	ç	35	40		2	18		20	32		39	40		43
Relative	constant	of solvent	(acetic	ac1d)+	Water	ed value)	6.88	,	7.06	7.25		7.62	o	D	8.38	0		9.80		13.5	20.8		28.1	35.4		42.7
Solvent	acid) con-	centration	8)				86	i	97.5	. 76		96	30	3	94	ç	2	93.75		88.75	78.75		68.75	58.75		48.75
Water	tration	(8)					1		1.25	1.5		7		?	т	u	n	יטו		10	20		05	40		20
HE con-	tion (%)	`		•			г		1.25	1.5	,	~		?	m	u	,	1.25		1.25	1.25	1	1.25	1.25		1.25
Relativ	dielect	ric	constan	יי סד	sorvent		6.15	ļ	6.13	6.15		6.15	21.2)	6.15	7 7	3	6.15		6.15	6.15	;		6.15		6.15
Solvent							Acetic	acid	Acetic	Acetic	acid	Acetic	acid	acid	Acetic	acid	acid	Acetic	acid	Acetic	Acetic	acid	Acetic	Acetic	acid	Acetic
							Ex. 9		PX: TO	Ex. 11		Ex. 12	13		Ex. 14	15		Ex. 16		Ex. 17	Ex. 18		EX. 13	Ex. 20		Ex. 21

HF-H20-tetrahydrofurane (THF) etchant

		_ •			4			,			
BPSG	/TE0	S	sèle	ctiv	ity	•		83	20	14	-
BSG/	TEOS	sele	ctiv	ity	·			130	16	10	α
BPSG	/THO	×	sele	ctiv	ity			110	. 27	19	
BSG/	THOX	sele	ctiv	ity				170	22	14	-
BPSG	etch	rate	(A/m	in.)				330	830	1200	1600
BSG	etch	rate	(A/m	in.)	·			210	069	890	1200
TEOS	etch	rate	(A/m	in.)	•			Þ	42	82	150
<u> </u>	_		(A/ E/A					3	31	64	
Relative	dielectric	constant of	solvent	(THF) +water	(calculated	value)		11.3	26.2	41.1	ה ה
Sol-	vent	(THE)	con-	cen-	tra-	tion	(8)	06	70	20	5
Water	-uoo	cen-	tra-	tion	(8)			5	22	45	ξ.
HF	-uop	cen-	tra-	tion	(8)			5	Ŋ	ĸ	ď
Relative	dielectric	constant	of solvent					7.6	7.6	7.6	ער
Sol-	vent			:				THE	THE	THE	THE
								22	23	24	25
				:				EX.	Ж Ж	EX.	<u>></u>

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BPSG	/TEO	တ	sele	ctiv	ity				63	18	11	6
BSG/	TEOS	sele	ctiv	ity					100	15	9.3	6.9
BPSG	/THO	×	sele	ctiv	ity				83	22	16	14
BSG/	THOX	sele	ctiv	ity					140	18	13	10
BPSG	etch	rate	(A/m	in.)					250	520	160	1300
BSG	etch	rate	(A/m	in.)	•				410	440	620	960
TEOS	etch	rate	(A/m	in.)					7	29	29	140
_		_	(A/a						3	24	49	96
Relative	dielectric	constant of	solvent	(acetone)+	water (cal-	culated	value)		23.7	35.9	48.0	60.1
Sol-	vent	(aceto	ne)	-uoo	cen-	tra-	tion	(%)	06	20	20	20
Water	con-	cen-	tra-	tion	(8)			:	S	25	45	3,5
HE	-uoo	cen-	tra-		æ)				2	S	s	r.
Relative	dielectric	constant	of solvent						20.7	20.7	20.7	20.7
Solvent									Ex. 26 Acetone	Acetone	28 Acetone	Acetone
									26	27	28	20
					:				EX.	EX.	ëx	<u>></u>

HF-H2O-acetone etchant

HF-H2O-methanol etchant

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olve.	Solvent Relative		Water	Solvent	Relative	THOX		BSG	BPSG	BSG/	BPSG	BSG/	BPSG	
	dielectric	-uoo	con-	(metha-	dielectric	etch	etch	etch	etch	THOX	/THO	TEOS	/TEO	
	constant		cen-	no1)	constant of	rate		rate	rate	sele	×	sele	ω,	
	of solvent		tra-	concen-	solvent	(A/m		(A/m	(A/m	ctiv	sele	ctiv	sele	
		tion	tion	tration	(metha-	in.)		in.)	in.)	ity	ctiv	ity	ctiv	
		(%)	(%)	(8) (8)	nol)+water						1ty		ity	
					(calculated									
					value)	•								
Methar	32.6	6	3	94	34.0	0.5	7	44	73	88	150	6.3	10	
Ex. 31 Methanol		2	s	96		m		170	230	57	77	19	56	_
12 1000		-	-	ă	30 0	22	43	730	410	33	6	1	ď	

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Solvent Relative dielectric constant of solvent	Ethanol
0 0	ď
Relative dielectric constant of solvent	24.6
	ۍ
Water con- cen- tra- tion (%)	5
Sol- vent (eth- anol) .con- cen- tra- tion (%)	06
Relative dielectric constant of solvent (ethanol)+ water [calculated value)	27.4
THOX etch rate (A/m in.)	7
etch rate (A/m in.)	6
BSG etch rate (A/m in.)	250
BPSG etch rate (A/m in.)	210
BSG/ THOX sele ctiv ity	36
THOX TEOS BSG BPSG BSG/ BPSG BSG/ BPSG etch etch etch THOX /THO TEOS /TEO rate rate rate sele X sele S (A/m (A/m (A/m (A/m (A/m (A/m (A/m (in.) in.) in.) ity ity ity ity	7 9 250 210 36 30
BSG/ TEOS sele ctiv ity	28
BPSG/TEO 'S sele ctiv ity	23

HF-H2O-ethanol etchant

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HF-NH4F-H2O etchant (Comparative Examples)

	•				•		•			,	•			
BPSG	/TE0	တ	sele	ctiv	ity			ı	_			1	-	1
BSG/	TEOS	sele	ctiv	ity	:			0.5	1.3	0.7	0.5	0.4	0.4	0.4
BPSG	/THO	×	sele	ctiv	∵ity			,	-	1		-	-	
BSG/	THOX	sele	ctiv	ity	•			9.0	2.2	1.4	6.0	9.0	9.0	6.0
BPSG	etch	rate	(A/m	in.)				-	1	•	•	1	1	1
BSG	etch	rate	(A/m	in.)	:			110	620	440	350	027	230	200
TEOS	etch	rate	(A/m	in.)				230	480	640	007	720	610	450
ТНОХ	etch	rate	(A/m	in.	<u>. </u>			170	280	320	400	420	390	300
Sol-	vent	(water	con-	cen-	tra-	tion	(8)	59.9	96	93	88	78	89	59.3
NH4F	con-	cen-	tra-	tion	(%)	•		39.1	2	2	01	20	30	38.7
l	-uoo			tion	. (8).			1	2	2	2	2	2	2
Relative -	dielectric	constant	of solvent					(78.3)	(78.3)	(78.3)	(78.3)	(78.3)	(78.3)	(78.3)
Solvent								(Water)	(Water)	(Water)	(Water)	(Water)	(Water)	(Water)
								Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8	Comp. Ex. 9	Comp. Ex.

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HF-H20-acid-added etchant Added pka of pka of pka of con- con- con- con- con- con- con- con-				<u>.</u>								_							
F-H2O-acid-added etchant Added pka of HF Water Acid THOX TEOS BSG BPSG BPSG BPSG BPSG BPSG BPSG acid con- concen etch etch etch etch THOX /THO cen- trate rate rate rate sele X tion tion tion in.) in.) in.) in.) in.) in.) in.) in.		BPSG	/TEO	s	sele	ctiv	ity		,	1	1	,	1	, .	;				
F-H2O-acid-added etchant Added pKa of HF Water Acid THOX TEOS BSG BPSG BSG/ acid con- con- concen etch etch etch THOX tra- tra- concen etch etch etch THOX tra- tra- n (%) (A/m (A/m (A/m (A/m (A/m (A/m (A/m (A/m		BSG/	TEOS	sele	ctiv	ity	:	14	13	13	14	12	16	6'5	S				
F-H2O-acid-added etchant Added pKa of HF Water Acid THOX TEOS BSG BPSG acid con- concen etch etch etch etch etch trate rate rate rate rate rate rate rat		BPSG	/THO	×	sele	ctiv	ity	1	ì	1	,	•	ı	1					
F-H ₂ O-acid-added etchant Added pKa of HF Water Acid THOX TEOS BSG acid acid con- concen etch etch etch trate tra- tra- tratio rate rate rate tion tion tion (%) (%) (%) (%) (%) (%) (%) (%) (%) (%)		BSG/	THOX	sele	ctiv	ity		97	23	21	24	19	22	4.8	7.1				
F-H ₂ O-acid-added etchant Added pKa of HF Water Acid THOX TEOS acid acid con- con- concen etch etch cen- traio rate rate tra- tra- n (%) (A/m (A/m tion tion in.) (%) (%) (%) (%) HCl -8 0.15 63.9 35.8 53 89 HCl -8 0.25 63.9 35.6 120 200 HCl -8 0.75 63.9 35.5 180 300 HCl -8 1 30.4 68.6 240 340 HCl -8 1 15.7 83.3 120 170 (pKa1) 7.20 (pKa2)		BPSG	etch	rate	(A/m	in.)		1	1	•	1	-					,		
F-H ₂ O-acid-added etchant Added pKa of HF Water Acid THOX acid con- con- concen etch tra- tra- ratio rate tron tion tion tion (%) (%) (%) (%) (%) (%) (%) (%) (%) (%)		BSG	etch	rate	(A/m	in.)		440	1200	2500	4300	4500	2300	850					
F-H ₂ O-acid-added etchant Added pKa of HF Water Acid acid acid con- concen central transport transport central transport central transport central c		TEOS	etch	rate	(A/m	in.)								170					
F-H ₂ O-acid-added etchant Added pKa of HF Water acid acid con- cen- tra- tra- tra- tra- tra- tra- tra- tra		THOX	etch	rate	(A/m	in.)	:	17	53	120	180	240	240	120					
F-H ₂ O-acid-added etchant Added pKa of HF acid control tra- trion (%) HCl -8 0.1 HCl -8 0.25 HCl -8 0.75 HCl -8 0.75 HCl -8 0.75 HCl -8 0.75 HCl -8 1 HCl -8 1 HCl -8 1 HCl -8 0.75 HCl -8 1 HNO3 -1.8 1 H3PO4 2.15 1	٠	Acid	concen	tratio	n (8)			35.9	35.8	35.6	35.5	35.3	9.89	83.3				_	
F-H ₂ O-acid-added etchar Added pKa of acid acid acid acid acid acid BCI -8 HCI -8 HC		Water	-uoo	cen-	tra-	tion	: (%)	64	63.9	63.9	63.8	63.7	30.4	15.7					
F-H ₂ O-acid-added Added pka o acid acid acid HCl -8 HCl	ant	HF	-uop	cen-	tra-	tion	(8)	0.1	0.25	0.5	0.75	Н	-1	r-4					
HF-H ₂ O-acid- Added acid acid Ex. 34 HCl Ex. 35 HCl Ex. 36 HCl Ex. 36 HCl Ex. 37 HCl		pKa of	acid				:	8-	8-	φ-	8-	8-	-1.8	2.15	(pKa1)	7.20	(pKa2)	12.4	(pKa3)
HE. 34 Ex. 35 Ex. 35 Ex. 36 Ex. 36 Ex. 37 Ex. 38 Ex. 39 Comp. Ex. 39	-H ₂ 0-acid-	Added	acid					HC1	HC1	HCI	HC1	HCI	HNO3	H3P04					
1	н							Ex. 34	Ex. 35	Ex. 36	Ex. 37		1	Comp. Ex.					

Claims

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- An etching solution comprising hydrofluoric acid, wherein a ratio of an etch rate of a boron silicate glass film (BSG)
 or boron phosphosilicate glass / an etch rate of a thermal oxide film (THOX) at 25°C is 10 or higher.
- 2. The etching solution according to claim 1, wherein a solvent in the etching solution has a relative dielectric constant of 61 or lower.
- 3. The etching solution according to claim 1, the solution containing at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom.
 - 4. The etching solution according to claim 1, the solution containing (i) water and (ii) at least one member selected from the group consisting of an organic acid and an organic solvent having a hetero atom, the water being contained in a concentration of 70% by weight or lower.
 - 5. The etching solution according to claim 1, wherein the weight ratio of HF: isopropyl alcohol: water is 0.1-50% by weight: 30-99% by weight: 0-70% by weight.
- 6. The etching solution according to claim 1, wherein the weight ratio of HF: acetic acid: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.
 - 7. The etching solution according to claim 1, wherein the weight ratio of HF: tetrahydrofuran: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.
- 8. The etching solution according to claim 1, wherein the weight ratio of HF: acetone: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.
 - 9. The etching solution according to claim 1, wherein the weight ratio of HF: methanol: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.
 - 10. The etching solution according to claim 1, wherein the weight ratio of HF: ethanol: water is 0.1-50% by weight: 30-99.9% by weight: 0-70% by weight.
 - 11. The etching solution according to claim 1, the solution comprising an inorganic acid.
 - 12. The etching solution according to claim 11, wherein the inorganic acid has a pKa value at 25°C of 2 or lower.
 - **13.** The etching solution according to claim 11, wherein the weight ratio of HF: HCI: water is 0.01-50% by weight: 1-36% by weight: 0-99% by weight.
 - 14. The etching solution according to claim 11, wherein the weight ratio of HF: HNO₃: water is 0.01-50% by weight: 1-70% by weight: 0-99% by weight.
- 15. A method for producing an etched article by etching an article to be etched with the etching solution as defined in any of claims 1-14.
 - 16. An etched article which is obtainable by the method of claim 15.

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INTERNATIONAL SEARCH REPORT

International application No.

		PC17	0199/06502
	IFICATION OF SUBJECT MATTER		
Int.			
1110.	C1 C09K 13700		
According to	International Patent Classification (IPC) or to both na	tional classification and IPC	
B. FIELDS	SEARCHED		
	ocumentation searched (classification system followed l C1 ⁷ H01L 21/306, 21/308	by classification symbols)	
1116.	CI HOLD 21/300, 21/308		
	ion searched other than minimum documentation to the		
Jits Koka	uyo Shinan Koho 1926-1996 i Jitsuyo Shinan Koho 1971-2000	Jitsuyo Shinan Toroku Toroku Jitsuyo Shinan	
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Electronic a	ata base consulted during the international search (name	e or data base and, where practicable, s	earch terms used)
C. DOCU	MENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where ap	propriate, of the relevant passages	Relevant to claim No.
-	JP, 52-56869, A (Tokyo Shibaura		110101111111111111111111111111111111111
	10 May, 1977 (10.05.77),		
X Y	Table 1; Fig. 3 Table 1; Fig. 3	•	1-5,9,10,15,16
	(Family: none)	•	12,14
Y	JP, 58-204540, A (Matsushita El	ectric Worke Ital	32.24
*	29 November, 1983 (29.11.83)		12,14
ł	Example 1		
A	EP, 669646, Al (Texas Instrumer	nts Inc.),	1-16
ł	30 August, 1995 (30.08.95),		
(Figs. 1 to 3 & JP, 7-240474, A & TW, 2881	58. A	
		·	
PA	EP, 887323, A1 (International Bu 30 December, 1998 (30.12.98),	siness Machines Corp.)	, 1-16
	Claims		1
l	& JP, 11-60275, A & CN, 1203:	205, A	
PA	JP, 11-74249, A (Samsung Electr	con Co., Ltd.).	1-16
	16 March, 1999 (16.03.99),		
Furthe	r documents are listed in the continuation of Box C.	See patent family annex.	
	Categories of cited documents:	"T" later document published after the i	nternational filing date or
conside	ent defining the general state of the art which is not ered to be of particular relevance	priority date and not in conflict with understand the principle or theory u	
"E" carlier	document but published on or after the international filing	"X" document of particular relevance; the considered novel or cannot be cons	he claimed invention cannot be
"L" docum	ent which may throw doubts on priority claim(s) or which is a establish the publication date of another citation or other	step when the document is taken ale	one
special	reason (as specified)	considered to involve an inventive	step when the document is
means	ent referring to an oral disclosure, use, exhibition or other	combined with one or more other so combination being obvious to a per	
	ent published prior to the international filing date but later to priority date claimed	"&" document member of the same pate	nt family
	actual completion of the international search	Date of mailing of the international s	earch report
09 I	February, 2000 (09.02.00)	22 February, 2000	(22.02.00)
	nailing address of the ISA/ anese Patent Office	Authorized officer	
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Facsimile N	lo.	Telephone No.	

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP99/06502

ategory*	Citation of document, with indication, where appropriate, of the releva-	nt passages	Relevant to claim No
	Claims (Family: none)	<u>-</u>	
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